

## Laboratory Formation and Characterization of Taranakite in a Hydrol Humic Latosol Soil from Hawaii<sup>1</sup>

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**ABSTRACT:** The mineral taranakite was obtained in reactions between samples of an Akaka soil and monopotassium phosphate solutions ranging from 0.2 to 0.6 molar, at pH values of the reacting system ranging from 2.3 to 2.9. Characteristics of the reaction products were compared with those of pure synthetic taranakite, using X-ray, chemical, optical, infrared absorption, and differential thermal techniques.

The taranakite was essentially a potassium-aluminum-phosphate complex. There was no indication of isomorphous substitution of iron for aluminum. The molar ratios of  $K/PO_4$  and  $Al/PO_4$  of the reaction product were found to be 0.37 and 0.72 respectively. The taranakite was thought to be formed by precipitation of a soluble phospho-alumino complex anion together with potassium ions.

The possibility is suggested of the formation of taranakite when soluble potassium and phosphate react with Hydrol Humic and Humic Latosols in the field. During the early stages of reaction, the reaction product is believed to be cryptocrystalline, but the size of crystals increases with time.

IN HAWAIIAN SOILS large amounts of added phosphate often are rendered at least temporarily unavailable to plants. Davis (1935) attributed this phenomenon to an absorption effect in the soils. He found that, for any given equilibrium phosphate concentration, the amount of phosphate fixed varies directly with the ratio of soil to solution. Chu and Sherman (1952) reported that, in the presence of hydrated iron and aluminum oxides, as much as 90% of added soluble phosphate was fixed by the soils in a relatively short period of time. When the oxides were removed, less than 30% of the applied phosphorus was fixed. The Hy-

drolic Humic Latosols showed the highest phosphorus-fixing capacities, but the Low Humic Latosols and Humic Latosols also fixed phosphorus to a considerable extent.

The manner in which phosphate is fixed in acid soils is as yet unknown, but in some instances it is likely to be in the nature of a solution-precipitation. Kittrick and Jackson (1955) reported, from electron microscope observations, that a solution-precipitation mechanism was operative in the reaction of phosphate with colloidal iron oxide particles and thin aluminum hydroxide films at room temperature. These authors also reported (1956) that there is a solution-precipitation mechanism operative in the reaction of phosphate with kaolinite and greenalite at room temperature. The reaction product in the potassium phosphate-kaolinite system was taranakite.

Several workers have identified phosphate complexes which could occur as reaction products in hydrous colloidal sesquioxide systems (Wada, 1959; Birrell, 1961; Lindsay et al., 1962; Tamimi et al., 1963; Tamimi, 1964). These phospho-reaction products have been associated with the presence of calcium, ammonium, and potassium cations in the system.

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Taranakite, or other similarly complex potassic aluminophosphate minerals, appears to be the most likely reaction product to be identified in soils to which potash and phosphate fertilizers have been added together or over a short time interval. In this study a search was made for the presence of taranakite in a highly aluminous soil to which potash and phosphate fertilizers had been added.

Records of naturally occurring taranakite are rare. Bannister and Hutchinson (1947) studied several native taranakite minerals, and pointed out that taranakite is usually found under moist conditions in localities where phosphate solutions from bird or bat guano react with rock or clay. The formula is given as



Taranakite is massive, claylike, pulverulent to compact; its color is white-gray or yellowish-white, and it is very soft and unctuous to the touch. This mineral was first found in 1865 on rocks which were being used for bird colonies at Sugarloaves, Taranaki, New Zealand. The minerals minervite (France) and palmerite (Italy) have been found to be identical with taranakite. Chemical analysis of the taranakite occurring at Sugarloaves, Taranaki, New Zealand (Dana, 1951), is as follows (in %):  $\text{K}_2\text{O}$ , 4.20;  $\text{CaO}$ , 0.55;  $\text{Al}_2\text{O}_3$ , 21.43;  $\text{P}_2\text{O}_5$ , 35.05;  $\text{H}_2\text{O}$ , 33.06; Insol., 0.80;  $\text{Cl}$ , 0.46;  $\text{SO}_3$ , trace;  $\text{FeO}$ , 4.45.

Murray and Dietrich (1956) also reported the occurrence of natural taranakite in a Virginia cave that was the home of a colony of bats. The taranakite was associated with brushite, a calcium phosphate mineral.

In artificial systems having soil constituents, crystalline phosphate products containing potassium and aluminum have been synthesized. Birrell (1961), in New Zealand, showed that the addition of monopotassium phosphate to allophane produces a taranakite, the X-ray diffraction pattern of which agreed well with the value given by Murray and Dietrich (1956). Lindsay et al. (1962) synthesized taranakite from Hartsells soil (from Tennessee) by adding monopotassium phosphate to the soil. Wada (1959) reported the identification of taranakite-like phosphate minerals resulting from the reaction of monoammonium phosphate

with allophane and halloysite. Lindsay et al. (1962) identified the reaction product of ammonium phosphate and Hartsells soil as ammonium taranakite. Tamimi et al. (1963) were able to identify an ammonium-taranakite by means of X-ray diffraction technique. The synthetic mineral was obtained from three Latosolic soils derived from volcanic ash—namely Akaka silty clay, Hilo silty clay loam, and Paauhau silty clay loam—by the addition of ammonium chloride or diammonium phosphate in the presence of phosphoric acid. The reaction products were similar to the taranakite-like minerals obtained by Wada from Japanese allophane and halloysite. Tamimi (1964) postulated that taranakite could form in soils having pH values ranging from 1.85 to 5.55, although no taranakite was identified in soils with a pH above 3.9. Haseman et al. (1950) also had indicated that synthetic taranakite is stable at pH values of about 1.7–5.3. Kittrick and Jackson (1956) found that taranakite can be formed at room temperature by the addition of molar potassium dihydrogen phosphate to kaolinite. Beaton et al. (1964) treated kaolinite with saturated, instead of one molar, monopotassium phosphate solution and found no evidence of taranakite formation.

In addition to chemical, optical, and X-ray methods, Arlidge et al. (1963) found that infrared spectroscopy and differential thermal analysis were valuable complementary methods to X-ray studies in the identification of taranakite and compounds of similar nature. Infrared spectroscopy, moreover, also gave information on their structure and degree of crystallinity.

#### MATERIALS

The sample selected for study was a subsoil of an Akaka silty clay loam taken from a steep road bank near the beginning of the forest reserve area on Kaiwiki Road, approximately 5 miles west of the main Hilo-Hamakua Highway on the island of Hawaii. Sampling depth was from 12 to 30 inches. The sample had a pH value of 5.5 and was a smeary clay. The soil was dominated by amorphous hydrous oxides of aluminum and iron. It also contained small amounts of crystalline gibbsite, goethite, magnetite, mica, and quartz (Tamura et al., 1953).

The main amorphous mineral colloid is allophane-like, excepting that the silica-to-alumina ratio is too low for the value of allophane proposed by Ross and Kerr (1934). The mineral is amorphous to X-rays, and differential thermal analysis indicates only a single, low temperature endotherm at about 180°C. It resembles so-called stable allophane (Jackson, 1956) in that it is resistant to decomposition by dilute hydrochloric acid of pH 3.5 or 2% sodium carbonate solution. Characteristics of the allophane-like fraction of Akaka soil and other amorphous mineral colloids are shown in Table 1.

The Akaka soil is a member of the Hydrol Humic Latosol Group, and was described by Cline et al. (1955). Akaka soils have developed from volcanic ash, under a tropical rain forest with an average annual rainfall of more than 120 inches. They are highly hydrated in the natural state; the water content sometimes exceeds 300% of the oven-dry weight of soil. The Akaka soils have very low bulk densities ranging from 0.1 to 0.6. On dehydration they lose volume and exhibit an increase in particles of sand size; the dehydration is irreversible. An explanation of this irreversibility has been given by Sherman (1957); he reported that the pro-

cess of dehydration caused the crystallization of the hydrous oxides to gibbsite, to crystalline iron oxide minerals, or to alpha quartz.

Monopotassium phosphate was used in the experiments. It is a product (reagent grade) of General Chemical Division, Allied Chemical Corporation. The pH of the phosphate solutions was adjusted with hydrochloric acid.

#### *Preparation of the Reaction Products for Characterization*

The reaction products were prepared by the following procedure. A 5–15 g sample of wet Akaka soil was placed in a 200-ml pyrex beaker or pyrex glass container of suitable size, to which was added 100 ml of potassium phosphate solution ranging from 0.2 to 0.6 molar, with an initial pH value of 2. The glass container was wrapped in a plastic bag and kept at room temperature (about 25°–30°C). The contents were filtered after standing from 1 to 200 days, and the pH of the filtrate was measured. The pH of the filtrate serves more or less as an indication of the pH of the reacting system, which, in turn, predicts the possible species of ions that enter into reaction. The residue was washed with 60% methanol, 80% ethanol,

TABLE 1  
CHARACTERISTICS OF THE ALLOPHANE-LIKE FRACTION OF AKAKA SOIL AS COMPARED  
WITH OTHER AMORPHOUS MINERAL COLLOIDS\* OF SOILS

| TYPE OF<br>AMORPHOUS<br>MATERIAL            | DIFFERENTIAL<br>THERMAL<br>INDICATION |           | SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> | SOLUBILITY<br>IN DILUTE<br>ACID AND<br>ALKALI |
|---|---------------------------------------|-----------|--|---|
|   | Endotherms                            | Exotherms |  |   |
|   | °C                                    | °C        |  |   |
| Allophane:                                  |                                       |           |  |   |
| unstable                                    | 150                                   | 960       | 0.3–2.0  | high  |
| stable                                      | 150                                   | 960       | 2.0  | low   |
| Silica                                      | 165–573                               | —         | —  | high  |
| Alumina                                     | 110–500                               | —         | —  | high  |
| Iron oxides                                 | 160                                   | 350–450   | —  | high  |
| Titanium<br>oxides                          | 195                                   | 465       | —  | low   |
| Allophane-like<br>fraction of<br>Akaka soil | 180                                   | —         | 0.8  | low   |

\* Jackson (1956:528).

and 95% ethanol by decantation (Wada, 1959) to remove excess phosphate. The finer fractions of the solid phase were collected on the filter paper. The coarser fractions were left in the glass container. Both fractions were then air-dried.

Potassium phosphate solutions having concentrations ranging from 0.2 molar to 0.05 molar, or from 0.6 molar to 1 molar, with initial pH values of 2–4, were also used, but crystalline reaction products did not form.

A taranakite sample was synthesized for comparison; the synthesis was made as follows: 20 ml of 65% phosphoric acid were mixed with an aluminum chloride solution containing 2.65 g of aluminum chloride. The mixture of phosphoric acid and aluminum chloride was filtered and diluted to 50 ml, and an aliquot was taken in a pyrex beaker and neutralized with 10% potassium hydroxide to a pH between 3.4 and 5.0. The beaker containing the flocculent precipitate was covered with a watch glass and kept in a 50°C water bath. The crystalline precipitate which formed was separated by filtration, washed with distilled water, and air-dried.

#### *Characterization of Phospho-reaction Products by X-ray Analysis*

The reaction products were identified by X-ray diffraction, using a Norelco X-ray diffractometer with copper  $K\alpha$  radiation. The X-ray diffraction patterns obtained throughout this study were of powder samples.

The effect of heating on the crystalline substance resulting from the soil-phosphate system and on the synthesized taranakite was examined. Both were subjected to a range of temperatures from 60°C to 150°C. The products resulting from heat treatment were identified by X-ray diffraction.

X-ray diffraction patterns of the phospho-reaction products prepared by treating Akaka soil with solutions containing potassium phosphate, ranging from 0.2 to 0.6 molar at pH 2, showed these reaction products to be taranakite. D-spacings for taranakite and heated taranakite obtained in these experiments and by Haseman et al. (1950) are gathered in Table 2. The prominent peaks of natural taranakites from

Sugarloaves, Taranaki, New Zealand, and from Pig Hole Cave, Giles County, Virginia, are at 16.2, 7.6, 3.82 Å, and at 15.49, 7.82, 3.79 and 3.12 Å, respectively. The 16.2 and 15.49 Å peaks are the strongest. The synthesized taranakite produced in this experiment, and those of Haseman et al. (1950), showed the strongest peak at 15.7 Å; and strong peaks at 7.89, 3.81, 3.14 and at 7.35, 3.79, 3.13 Å, respectively. Except for the 7.89 Å peak given by the phospho-reaction product obtained from Akaka soil, the prominent peaks of natural and synthesized taranakite are similar to the reaction products obtained from the Akaka soil. Birrell (1961) identified a taranakite by treating a Tirau ash-slay fraction from New Zealand with potassium phosphate solution. The X-ray diffraction pattern of the taranakite studied by Birrell showed prominent peaks at 15.60, 3.81, and 3.13 Å, and is very similar to that of the phospho-reaction products obtained from the Akaka soil.

The reaction products resulting from soil-phosphate systems, and the synthesized taranakite, were heated to different temperatures in order to examine the dehydration products, as well as the effect of heating on crystallinity. The dehydration products resulting from the soil-phosphate systems and the synthesized taranakite were similar with d-spacings of 13.6, 6.8, 5.5, and 3.4 Å. This substance is a compound like Product B as synthesized by Haseman et al. (1950). Both the reaction product resulting from soil-phosphate systems and the synthesized taranakite became amorphous above 130°C.

#### *Characterization of Phospho-Reaction Products by Chemical Analysis*

The evaluation of  $K/PO_4$  and  $Al/PO_4$  ratios for the reaction product was difficult because of contamination of the reaction product by soil particles. Therefore, a factorial experimental design (Snedecor, 1956) with four replications at three levels of soil was prepared, using 5, 10, and 15 g samples of wet soil with a 0.4 molar potassium phosphate solution at pH 2. Phosphate was estimated by chlorostannous-reduced molybdophosphoric blue color in a hydrochloric acid system, following fusion of the sample with sodium carbonate, and decom-

TABLE 2  
POWDER X-RAY DIFFRACTION PATTERNS OF THE HEAT-TREATED REACTION PRODUCTS, SYNTHESIZED TARANAKITE  
AND PRODUCT B OF HASEMAN ET AL. (1950)

| PHOSPHO-REACTION PRODUCTS PRODUCED FROM AKAKA SOIL, DAYS OF STANDING |      |        |      |       |       |   |      |   |       |       |       |       |       |       |       |       |
|--|------|--------|------|-------|-------|---|------|---|-------|-------|-------|-------|-------|-------|-------|-------|
| 5  |      |        | 54   |       |       |   | 200  |   |       |       |       |       |       |       |       |       |
| 70 C   |      | 120 C  | 90 C |       | 105 C |   | 90 C |   | 100 C |       | 110 C |       | 120 C |       | 130 C |       |
| d  | d    | Ch. I* | d    | Ch. I | d     | I | d    | I | d     | Ch. I | d     | Ch. I | d     | Ch. I | d     | Ch. I |
| 7.43   | 13.6 |        | 15.7 | ↓     | 13.6  | S | 13.6 | S | 13.6  |       | 13.6  | ↑     | 13.6  | ↑     | 13.6  | ↓     |
| 5.53   | 7.43 | ↓      | 13.6 |       | 7.37  | M | 7.43 | S | 7.43  | ↓     | 7.43  | ↓     | 7.43  | ↓     | 7.43  | ↓     |
| 4.29   | 5.53 | ↓      | 7.37 |       | 6.86  | M | 7.08 | W | 7.08  |       | 7.08  | ↓     | 7.08  | ↓     | 6.86  | ↓     |
| 3.40   | 4.33 |        | 5.55 |       | 5.55  | M | 6.86 | W | 6.86  | ↑     | 6.86  | ↑     | 6.86  | ↑     | 5.57  | ↓     |
| 3.33   | 4.15 |        | 4.29 | ↑     | 4.33  | M | 5.57 | M | 5.57  | ↑     | 5.57  | ↓     | 5.57  |       | 3.40  | ↓     |
| 3.03   | 3.40 | ↑      | 4.15 |       | 4.15  | M | 4.35 | M | 4.29  |       | 4.31  | ↑     | 4.31  | ↑     |       |       |
| 2.81   | 3.33 | ↓      | 3.40 |       | 3.66  | W | 4.31 | M | 4.15  |       | 4.15  |       | 4.15  | ↑     |       |       |
|  |      |        | 3.15 |       | 3.61  | W | 4.15 | M | 3.66  |       | 3.67  |       | 3.69  | ↓     |       |       |
|  |      |        | 2.91 |       | 3.40  | S | 3.69 | W | 3.40  | ↑     | 3.54  | ↓     | 3.54  | ↓     |       |       |
|  |      |        | 2.81 | ↓     | 3.15  | M | 3.40 | S | 3.16  |       | 3.40  | ↑     | 3.40  | ↓     |       |       |
|  |      |        |      |       | 3.02  | W | 3.16 | W | 3.03  |       | 3.16  |       | 3.16  |       |       |       |
|  |      |        |      |       | 2.90  | W | 3.03 | M | 2.91  | ↑     | 3.13  |       | 3.03  | ↑     |       |       |
|  |      |        |      |       | 2.77  | W | 2.91 | M | 2.81  |       | 2.91  | ↑     | 2.91  | ↑     |       |       |
|  |      |        |      |       |       |   | 2.80 | M | 2.77  | ↑     | 2.81  |       | 2.77  |       |       |       |
|  |      |        |      |       |       |   | 2.77 | M |       |       |       |       | 2.69  |       |       |       |
|  |      |        |      |       |       |   |      |   |       |       |       |       | 2.66  |       |       |       |

\* Change in intensity:    ↑ represents increase in intensity.

                                 ↓ represents decrease in intensity.

Note: Prominent peaks of dehydrated taranakite are underlined.

TABLE 2 (Continued)

| SYNTHESIZED TARANAKITE |        |             |       |             |       |             |   |             |       | PRODUCT B OF<br>HASEMAN ET AL. |                     |
|------------------------|--------|-------------|-------|-------------|-------|-------------|---|-------------|-------|--------------------------------|---------------------|
| 70 C                   |        | 80 C        |       | 90 C        |       | 100 C       |   | 130 C       |       | d                              | I/I <sub>1</sub> ** |
| d                      | Ch. I* | d           | Ch. I | d           | Ch. I | d           | I | d           | Ch. I |                                |                     |
| 15.7                   | ↓      | 15.7        | ↓     | 15.7        | ↓     | <u>13.6</u> | S | <u>13.6</u> | ↓     | 13.8                           | 1.00                |
| 7.89                   | ↓      | <u>13.8</u> |       | <u>13.6</u> | ↑     | <u>7.37</u> | M | <u>7.37</u> | ↓     | 7.35                           | .68                 |
| 7.43                   |        | <u>7.89</u> | ↓     | <u>7.43</u> | ↑     | <u>6.80</u> | M | <u>6.80</u> | ↑     | 6.79                           | .51                 |
| 5.86                   | ↓      | 7.43        | ↑     | <u>5.53</u> | ↑     | <u>5.53</u> | M | <u>5.53</u> |       | 6.05                           | .15                 |
| 4.31                   |        | 5.81        | ↓     | <u>4.29</u> | ↑     | <u>4.29</u> | M | <u>4.29</u> | ↓     | 5.46                           | .68                 |
| 4.14                   |        | <u>5.57</u> |       | 4.13        | ↑     | 4.13        | M | 4.13        | ↓     | 4.26                           | .40                 |
| 3.80                   | ↓      | 4.31        |       | 3.57        |       | 3.66        | W | 3.66        | ↓     | 4.14                           | .51                 |
| 3.73                   |        | 4.13        | ↑     | <u>3.40</u> | ↑     | 3.53        | W | <u>3.40</u> | ↓     | 3.89                           | .04                 |
| 3.72                   |        | 3.80        | ↓     | 3.13        |       | <u>3.40</u> | S | <u>3.14</u> | ↓     | 3.64                           | .24                 |
| 3.57                   | ↓      | 3.73        | ↓     | 2.91        | ↑     | 3.14        | M | 3.03        | ↓     | 3.50                           | .16                 |
| <u>3.40</u>            |        | 3.72        | ↓     | 2.84        |       | 3.03        | M | 2.91        |       | 3.39                           | 1.00                |
| 3.35                   | ↓      | 3.57        | ↓     | 2.81        |       | 2.91        | M | 2.81        | ↓     | 3.13                           | .49                 |
| 3.29                   | ↓      | <u>3.40</u> | ↑     |             |       | 2.81        | M | 2.77        | ↓     | 3.01                           | .40                 |
| 3.13                   | ↓      | 3.13        |       |             |       | 2.77        | M |             |       | 2.90                           | .64                 |
| 2.84                   |        | 2.91        |       |             |       |             |   |             |       | 2.84                           | .11                 |
| 2.81                   | ↓      | 2.84        |       |             |       |             |   |             |       | 2.79                           | .38                 |
| 2.73                   | ↓      | 2.81        | ↓     |             |       |             |   |             |       | 2.76                           | .40                 |
| 2.62                   | ↓      |             |       |             |       |             |   |             |       | 2.74                           | .25                 |
|                        |        |             |       |             |       |             |   |             |       | 2.68                           | .16                 |
|                        |        |             |       |             |       |             |   |             |       | 2.64                           | .24                 |
|                        |        |             |       |             |       |             |   |             |       | 2.56                           | .09                 |

\* Change in intensity.

\*\* Visual estimates of peak intensities.

Note: Prominent peaks of dehydrated taranakite are underlined.

position of the melt with hydrochloric acid (Jackson, 1958). Potassium was determined by the flame photometer method, using a Model 21 Coleman Flame Photometer. Aluminum was analyzed by Chenery's colorimetric method, as modified by Moomaw et al. (1959). The entire experiment was repeated 10 times. A homogeneity test was conducted using the M-value as the criterion (Hartley, 1944). In its final form, the M-test involves computing

$$M = (n_1 + n_k) \log_e \frac{n_1 s_1^2 + \cdots + n_k s_k^2}{n_1 + \cdots + n_k} \\ - (n_1 \log_e s_1^2 - n_k \log_e s_k^2)$$

where there are  $k$  samples,  $n_1, \dots, n_k$ , are the respective degrees of freedom and  $s_1^2, \dots, s_k^2$  the respective estimates of variance. The homogeneity test showed that 3 of the 10 experiments were not homogeneous with the others and therefore they were rejected. Data obtained from the 7 remaining experiments were combined. Analysis of variance with respect to the ratios  $K/PO_4$  and  $Al/PO_4$  were carried out. The amounts of soil used did not affect significantly the ratios  $K/PO_4$  or  $Al/PO_4$ .

The possibility of isomorphous substitution of iron for aluminum in the reaction product, under the conditions of investigation, was also examined. Relatively pure crystalline reaction products were selected and were ignited over a Meker Burner. When ignited, the crystals should show a reddish color if iron-substituted taranakite is present. This did not occur; upon ignition, the iron-containing compounds gave hematite.

The average values of  $K/PO_4$  and  $Al/PO_4$  obtained from the seven experiments were considered to be taken from a representative sample because the M-test proved to be nonsignificant. The molar ratios of  $K/PO_4$  and  $Al/PO_4$  for the reaction products were 0.37 and 0.72, respectively. Those for the synthesized taranakite were 0.37 for  $K/PO_4$  and 0.60 for  $Al/PO_4$ . These values are very close to the ones calculated from the formula of taranakite established by Smith and Brown (1959), which is 0.38 for  $K/PO_4$  and 0.63 for  $Al/PO_4$ . The molar ratio  $Al/PO_4$  for the reaction products is somewhat higher because the reaction prod-

ucts from the soil-phosphate systems were contaminated with Al-containing soil particles.

From the preceding experiments it is clear that the active constituent reacting with phosphate in Akaka soil is aluminum rather than iron. Recent work on the precipitation of phosphate in acid soils by Taylor et al. (1964) also revealed that aluminum hydroxide is the principal reagent in the precipitation of phosphate from fertilizers in acid soils.

#### *Characterization of Phospho-reaction Products by Optical Methods, Infrared Analysis, and Differential Thermal Analysis*

Optical properties of the reaction products from the soil-phosphate systems and from synthesized taranakite were determined. In addition to the synthesized taranakite already described, a second synthetic preparation was prepared as follows: 10 ml. of 1.5 molar monopotassium phosphate solution was mixed with a solution containing 0.25 g aluminum by vigorous stirring. The pH of this mixture was adjusted to 4.0 with 10% potassium hydroxide. The precipitates formed were kept in water at 50°C for a period of time. They were then filtered, washed with distilled water, and air-dried.

Immersion liquids were used to determine refractive indices. Other optical properties were studied by using thin sections of minerals mounted in Lakeside 70 Transparent Cement.

When examined under the polarizing microscope, both the reaction products obtained from the soil-phosphate systems and the synthesized taranakite were biaxial negative with a very small value of  $2V$ . The refractive indices determined for the phospho-reaction product were  $n_\alpha = 1.504$ ,  $n_\beta = 1.507$ ,  $n_\gamma = 1.509$ , and  $n_\gamma - n_\alpha = 0.005$ . Those for the synthesized taranakite were:  $n_\alpha = 1.503$ ,  $n_\beta = 1.505$  and  $n_\gamma = 1.506$ ,  $n_\gamma - n_\alpha = 0.003$ . These values are in reasonable agreement with those obtained by Haseman et al. (1950). The crystals are colorless and occur as tiny columnar aggregates. The aggregates of crystals tend to grow together, perpendicular to each other in pairs, to form a twinlike crystal in a rosette pattern, displaying a pseudohexagonal outline.

Smith and Brown (1959) re-examined the



synthesized taranakite prepared by Haseman et al. (1950) and considered that the taranakite was hexagonal and uniaxial negative. In the original report Haseman et al. described their synthesized product as pseudohexagonal and biaxial negative. It seems that taranakite might exist dimorphously, with 2V values ranging from 0 to about 20 degrees.

Infrared analyses of the phospho-reaction product and the synthesized taranakite were carried out. The phospho-reaction product from the Akaka soil was formed with 0.4 molar potassium phosphate, at pH 2, and 5 g of wet soil. The reacting system was left to stand for 200 days before the reaction product was collected. Purification of the phospho-reaction products was conducted by repeated reprecipitation with potassium hydroxide in phosphoric acid solution. The samples were ground, mixed with potassium bromide, and pressed into discs, and infrared spectra were obtained using a Beckman infrared spectrophotometer.

The infrared spectra of the phospho-reaction product produced from Akaka soil, and of the synthesized taranakite, in pressed KBr discs, were in good correspondence with each other. The patterns obtained are shown in Figure 1. Absorption peaks near  $3400\text{ cm}^{-1}$  showed the presence of water of crystallization. Corbridge and Lowe (1954) reported that all hydrated salts absorb in the  $3300\text{-cm}^{-1}$  and  $1640\text{-cm}^{-1}$  regions, which presumably correspond to O-H stretching and O-H bending, respectively. Complex phosphate absorption bands between  $1200\text{ cm}^{-1}$  and  $870\text{ cm}^{-1}$  and P-OH linkages near  $2500\text{ cm}^{-1}$  indicated the presence of  $\text{PO}_4^{3-}$  and acidic phosphate ions, respectively (Corbridge, 1956). These values are very close to the infrared absorption spectrum for taranakite obtained by Arlidge et al. (1963).

Differential thermograms of the phospho-reaction product and the synthesized taranakite samples were obtained. The differential thermal setup is the same as the one described by Uehara and Sherman (1956).

The differential thermal curves show that both the phospho-reaction product produced from the Akaka soil and the synthesized taranakite undergo endothermic reactions at about  $230^\circ\text{C}$  and exothermic reactions between  $500^\circ$

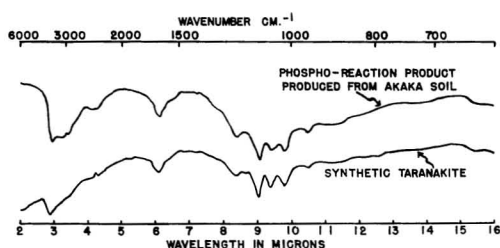


FIG. 1. Infrared absorption spectra of soil-phosphate reaction product and pure synthesized taranakite.

and  $600^\circ\text{C}$ . These differential thermal curves, which are shown in Figure 2, indicate that the phospho-reaction products from Akaka soil and the synthesized taranakite both lose their water of crystallization in one stage, as evidenced by the endotherm at  $230^\circ\text{C}$ . Arlidge et al. (1963) found similar peaks from samples supplied by the Tennessee Valley Authority, but natural taranakite from Pig Hole Cave and a synthetic taranakite lost their water of crystallization in two stages. This variation is thought to be associated with variations in degree of crystallinity of particle size. The exothermic peak between  $500^\circ\text{C}$  and  $600^\circ\text{C}$  probably represents the recrystallization of the mineral after it has been dehydrated, as suggested by Murray and Dietrich (1956). The differential thermal gravimetric curves for taranakite obtained by Arlidge et al. (1963) revealed that there is no weight change during the process of exothermic reaction, indicating the possibility of recrystallization.

The fact that all the taranakite samples studied in this experiment are amorphous to X-rays when they are heated above  $130^\circ\text{C}$  shows that the recrystallized products from dehydrated taranakite are too small or too poorly ordered to be identified by X-ray diffraction.

#### *The Effect of Time on Crystallite Size of the Phospho-reaction Product Produced from the Akaka Soil*

The relationship,  $n\lambda = 2d\sin\theta$ , deduced by Bragg, describes the conditions under which electromagnetic waves reflected from a set of planes in a crystal will be in phase with each other. The relationship requires that the planes be semi-infinite in the two dimensions perpen-



dicular to the normal about which the waves are reflected.

For crystals or particles below  $20\mu$  in diameter, this requirement is no longer fulfilled and deviations from the Bragg equation become apparent. As the crystals or particles get smaller, the deviations become larger; they are shown in X-ray diffraction patterns by an increasing broadening of the recorded reflections. Conversely, the breadth of the reflections can be used as a measure of particle size. The methods by which this may be done are described in any standard text on X-ray diffraction methods (see Henry, Lipson, and Wooster, 1951). The effect of time of crystallization on crystallite size may be studied by these methods. In this study 5-g portions of the wet Akaka soil were treated as follows: (a) With 0.4 molar potassium phosphate at pH 2. The reaction system was left to stand for 5, 54, and 200 days. The finer fraction of the solid phase was filtered, washed, and dried, as usual. The half-peak breadths of the  $15.7\text{ \AA}$  peaks were measured and were plotted (log scale) against time. (b) With 0.5 molar potassium phosphate at pH 2 for 6, 10, and 15 days. The preparations were washed and dried as before. The half-peak breadths of the  $15.7\text{ \AA}$  peaks were plotted (log scale) against time of preparation. The results are shown in Figure 3. The crystal size of the taranakite increases with time, in accordance with expectation.

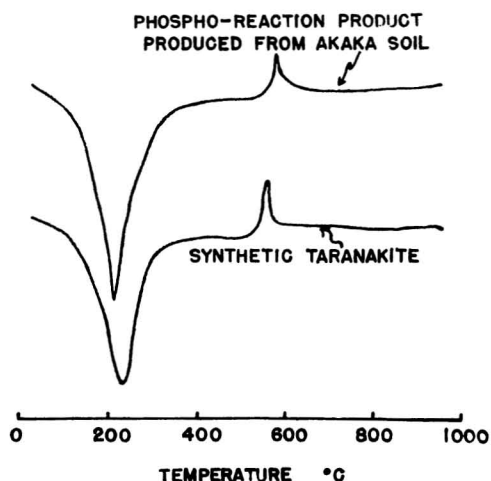


FIG. 2. D.T.A. curves of soil-phosphate reaction product and pure synthesized taranakite.

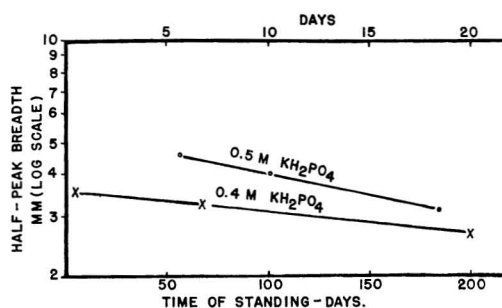


FIG. 3. Relationships between crystal size as measured by half-peak breadth and time of preparation.

#### DISCUSSION

Clearly identifiable taranakite was produced under the conditions of the experiments; that is, with weights of soil varying from 5 to 15 g, and with 0.2 to 0.6 molar solutions of potassium phosphate adjusted to pH 2. The pH values of the filtrate, and presumably of the reacting system, varied from pH 2.3 to 2.9. Many other concentrations of potassium phosphate and other pH values were tried, but nowhere outside and above that range was crystalline taranakite detected.

Chemical analysis gave  $K/PO_4$  and  $Al/PO_4$  ratios close to those obtained with synthetic samples, although the results for  $Al/PO_4$  did show that some contamination of the crystals with soil material had occurred. The contamination did not cause significant differences to appear between infrared patterns or differential thermograms of soil-derived and synthetic taranakites.

The taranakite was probably formed by a series of reaction steps. The initial step would be the dissolution of  $Al^{3+}$  ions from the amorphous, hydrous oxides, followed by the formation of a complex anion by reaction between  $Al^{3+}$  and  $H_2PO_4^-$ , and finally by precipitation with  $K^+$  ions. Although the  $Al^{3+}$  ions will be hydrated in solution, the infrared and differential thermal patterns indicate that water is not a structural constituent of the complex anion.

No crystalline taranakite was detected at the pH values which are common to Akaka soils in the field. However, from the evidence obtained here and from a review of the literature, it is reasonable to suppose that a cryptocrystalline

form of taranakite is formed when heavy applications of fertilizers containing potassium phosphate are made to soils of the Hydrol Humic and Humic Latosol groups. Current applications by sugar cane producers range as high as 175 lb of P and 600 lb of K per acre for each planting or ratoon crop. Because of the heavy rainfall the soils are continually wet. Concentrated solutions of potassium phosphate have a pH of 4, at which value  $\text{Al}^{3+}$  cations and  $\text{H}_2\text{PO}_4^-$  anions exist in solution. Many times during the decomposition of the applied fertilizer, the concentrations will rise high enough in the subsurface horizons of the soil to enable cryptocrystalline precipitates to form. With time these precipitates can be expected to grow into larger and better-ordered crystals of taranakite.

#### CONCLUSIONS

1. Crystalline taranakite formed when the Akaka soil was treated with potassium phosphate solutions ranging from 0.2 to 0.6 molar and the pH value of the reacting system ranged between 2.3 and 2.9. On heating, the phosphate reaction products and a synthesized taranakite gave similar dehydration products.

2. The taranakite was essentially a potassium-aluminum-phosphate complex. There was no indication of isomorphous substitution of iron for aluminum. The molar ratios of  $\text{K}/\text{PO}_4$  and  $\text{Al}/\text{PO}_4$  for the reaction product were estimated to be 0.37 and 0.72, respectively, which agreed well with values found for the synthetic mineral.

3. Optical analysis showed that the taranakite crystals were colorless and pseudohexagonal in form. They were biaxial negative. The refractive indices were  $n_\alpha = 1.504$ ,  $n_\beta = 1.507$  and  $n_\gamma = 1.509$ , respectively,  $n_\alpha - n_\gamma = 0.005$ .

4. Structural diagnosis by means of infrared spectroscopy of the potassium-aluminum-phosphate complex revealed that water of crystallization,  $(\text{PO}_4)^{3-}$  ions, and P-OH linkages were all present.

5. Differential thermal data showed that both the phospho-reaction product and the synthesized taranakite underwent an endother-

mic reaction at about 230°C, and an exothermic reaction between 500°C and 600°C.

6. It is proposed that potassium and phosphate ions from heavy applications of fertilizer may react with aluminum ions in soil solutions in the subsoils of Hydrol Humic and Humic Latosols to produce cryptocrystalline precipitates which, with time, will grow and transform into crystalline taranakite.

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